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<b>(21) International Application Number:</b> PCT/US97/05298 <b>(22) International Filing Date:</b> 1 April 1997 (01.04.97)  <b>(30) Priority Data:</b> 08/626,640                      2 April 1996 (02.04.96)                      US  <b>(71) Applicant:</b> TECHNEGLAS, INC. [US/US]; 25875 State Route 25, 52 LDP, Perrysburg, OH 43551 (US). <b>(71)(72) Applicant and Inventor:</b> PEER, Joseph [US/US]; 312 Wakefield Place, Oregon, OH 43616 (US). <b>(74) Agents:</b> JACQUES, Laurie, N. et al.; Porter, Wright, Morris & Arthur, 41 South High Street, Columbus, OH 43215 (US).		<b>(81) Designated States:</b> CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SEALING GLASS MODIFIER FOR USE WITH VOC-FREE OR LOW-VOC VEHICLE  <b>(57) Abstract</b>  A sealing glass modifier that decreases the chemical reduction of PbO in a PbO-containing sealing glass to metallic lead during sealing or firing, and enables the sealing glass to be used in combination with a VOC-free or low-VOC vehicle. The modifier preferably comprises an inorganic nitrate that is thermally stable at the temperatures at which the sealing glass frit seals the glass surfaces together, but that can be reduced to a lower oxidation state when exposed to the reducing conditions. The modifier is added to the sealing glass system in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired in the presence of reducing conditions at a temperature sufficient to seal the glass. Particularly preferred modifiers are $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and/or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The modifier may be incorporated as a component of the sealing glass. Alternatively, the modifier may be dissolved or dispersed in the vehicle.		

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## SEALING GLASS MODIFIER FOR USE WITH VOC-FREE OR LOW-VOC VEHICLE

### BACKGROUND AND OBJECTS OF THE INVENTION

The present invention is concerned generally with sealing glass compositions, in powdered form or admixed with a vehicle to form a sealing glass paste, for sealing glass components such as television picture tubes. The invention renders a PbO-containing sealing glass suitable for use in combination with a vehicle that includes much lower levels of volatile organic compounds ("VOC") than conventional vehicles. The sealing glass modifier of the present invention therefore allows the sealing process to be carried out with low or no VOC emissions when the vehicle is volatilized during the sealing process.

PbO-containing sealing glasses, and particularly PbO/B<sub>2</sub>O<sub>3</sub>/ZnO sealing glasses, are commonly used commercially to seal the glass face plate to the glass funnel of a cathode ray tube, such as a color television picture tube. Such sealing glasses have the property of melting and flowing at low temperatures, *i.e.*, usually below 500° C. and most frequently between 440° C. and 475° C., which facilitates the wetting of the glass surfaces to be sealed. These sealing glasses (sometimes referred to as "solder" glasses) are customarily thermally devitrifiable or thermally crystallizable in nature. The devitrified or crystallized glass has a melting point temperature that is higher than the fiber softening point temperature of the original sealing glass. Seals produced using these sealing glasses must have a suitable combination of properties to perform satisfactorily in television

picture tubes and the like. These properties include appropriate thermal expansion characteristics to avoid damage to the tube components, good flow to produce proper fillet shape, good wetting to provide strong adhesive characteristics to the glass parts being sealed, and good crystallization properties to allow formation of a strong crystallized seal within a reasonable thermal soak time. The seals also must have good dielectric characteristics to prevent failure of the tube when it is exposed to high voltages during use.

Before the face plate and funnel are sealed together, each undergoes a number of processing steps. These steps include the separate and successive application to the face plate of green, blue and red phosphors by known techniques, with the phosphors being present as a multiplicity of individual dots or stripes in an ordered arrangement on the inner surface of the face plate. In some instances, a carbon or graphite background may be applied to the inner surface of the face plate surrounding the phosphors and providing a sharp contrast to the phosphors. A resinous or plastic film may be applied to the surface of the phosphors, and the inner surface of the face plate is subsequently aluminized, *i.e.*, a thin aluminum film is deposited, so that an electrically conductive surface is formed. This aluminized surface is connected to a metal stud on the inner surface of the face plate.

A number of different organic compounds usually are applied to the inner surface of the face plate during the course of phosphor application and aluminization. As described further below, these compounds must be subsequently volatilized or otherwise removed from the face plate or face panel to decrease the natural tendency of the PbO constituent in the sealing glass to be reduced to metallic lead during firing of the glass seal. Such removal is accomplished by known take out or bake out processes.

After the preparatory face plate and funnel processing steps have been completed, a sealing glass is applied to the mating edge surfaces of the funnel. The components are assembled, fired in a nonreducing atmosphere at a temperature that is sufficiently elevated to fuse the sealing glass (*ie.*, about 425° C. to about 475° C.), and then cooled, thereby resulting in the formation of a strong, adherent hermetic bond of devitrified or crystallized sealing glass between the face plate and funnel components.

After the face plate has been sealed to the funnel portion of the tube, the interior confines of the tube are evacuated by applying a vacuum thereto. The tube must be heated to a temperature within the range of about 300° C. to about 410° C. while being evacuated to assure that all volatile substances, such as moisture and organic materials, are liberated and withdrawn from the interior surfaces and confines of the tube. The application of heat to the tube inevitably results in some relational shifting of the face plate, funnel and solder glass seal with respect to each other. Thus, a strong devitrified seal is necessary to withstand the creation or concentration of physical stresses in the vicinity of the seal resulting from the relational shifting of parts during the heating operation and subsequent cooling.

The PbO constituent in the sealing glass has a natural propensity or tendency to be reduced to metallic lead during the course of heat sealing in a reducing atmosphere or in the presence of organic vapors. This reduction of the PbO constituent tends to induce dielectric breakdown in the resultant seal when the resultant seal is exposed to high voltage conditions such as those existing within a color television tube during its operation. Because the high voltages present in a television tube during its operation in a television set range from about 25 kV to 45 kV or more for a color television tube, any

dielectric breakdown in the seal between the funnel and face plate will provide a source of tube malfunctions. A tube with appreciable amounts of metallic lead in its seal is unacceptable for use, and is likely to be rejected when the tube undergoes a standard voltage test conducted at the tube manufacturing plant. Consequently, special precautions must be taken by television tube manufacturers to prevent any such reduction of PbO during the sealing process. Seals in which the PbO constituent has been reduced are gray or gray-black in color, indicating the presence of metallic lead, rather than the yellow color that is characteristic of devitrified PbO glass.

Sealing glasses typically are applied to the mating edge surfaces of the funnel in paste form. The paste is made by combining the sealing glass with a vehicle that holds the glass frit in a ribbon form for a period of time sufficient to enable the resultant paste to be applied to one of the mating pieces, *e.g.*, in the case of a color television tube, the funnel, and the mating pieces, *e.g.*, the face plate and funnel, to be joined and sealed. The vehicle constituents must be pyrolyzable when they are subjected to a temperature below the temperature at which the sealing glass frit is fired and must leave only an inappreciable amount, if any, of residue in the fired frit.

Conventional vehicles generally comprise a binder and a solvent. The only binder that has achieved widespread commercial success in vehicles for PbO-containing sealing glasses, such as the PbO/B<sub>2</sub>O<sub>3</sub>/ZnO sealing glasses, is nitrocellulose (usually as a 1 to 1.4% solution in amyl acetate or butyl acetate). Although other compounds, such as ethyl cellulose and hydroxypropyl cellulose, may be used as binders for PbO-containing sealing glasses, nitrocellulose is particularly preferred because it tends to decrease the reduction of the PbO constituent to metallic lead during the sealing process. As described further

below, this contributes to the formation of satisfactory seals between the tube components.

Amyl acetate and butyl acetate are the preferred solvents for use in sealing glass vehicles because they volatilize rapidly from the extruded ribbon, thus permitting the ribbon to be fired more quickly to seal the adjoining glass surfaces. They also are excellent solvent for nitrocellulose. Ethylene glycol methyl ether also is a suitable binder solvent, either alone or in admixture with the amyl acetate. Ethylene glycol ethyl ether, methyl amyl acetate, ethyl hexyl acetate, n-butyl acetate, isobutyl acetate, sec-butyl acetate and diethylene glycol monobutyl ether acetates are other examples of the many binder solvents that may be used. The amount of solvent in the paste will depend upon the desired paste consistency, but will usually comprise about five to about fifteen weight percent of the paste.

The amount of vehicle necessary for the paste is the amount that will maintain the sealing glass frit in a wet form, extrudable as a bead or ribbon that holds its extruded shape for the necessary length of time. The ribbon must be wide enough to produce an effective and acceptable seal but less than the width of the funnel edge to avoid excess paste being squeezed out from between the adjoining surfaces of the funnel and face plate during the sealing process. However, the ribbon The width of the extruded ribbon and the weight of the ribbon being extruded for a given length may vary appreciably over time during the course of application of a single batch of paste. Thus, the operator of the dispensing apparatus must carefully monitor the ribbon and adjust the volume of the paste being extruded as needed to keep the width and the weight of the ribbon substantially uniform from the orifice of the dispensing apparatus onto and completely about the

periphery of the funnel edge. The weight ratio of sealing glass solids (including refractory fillers, nucleating agents, and any modifiers) to vehicle is usually in the range of about 8.0:1 to about 16.0:1, and preferably about 11.0:1 to about 13.0:1, for conventional vehicles. Preferably, the paste obtained by combining the vehicle with the sealing glass is reasonably stable for at least three to four hours or more so that the paste can be made in acceptably large quantities.

Because use of nitrocellulose as a binder for PbO-containing sealing glasses tends to decrease the reduction of the PbO constituent to metallic lead during the sealing process, seals formed from pastes that employ nitrocellulose as a binder are less susceptible to dielectric breakdown caused by the reduction of PbO to metallic lead. The nitrocellulose is thought to provide a source of oxygen during heating of the sealing glass that decreases the likelihood and extent of PbO reduction. Other binders do not offer the advantage of decreasing the tendency of the PbO in the sealing glass to be reduced to metallic lead. For example, the thermal decomposition of hydroxypropyl cellulose results in the liberation of organic compounds that are capable of chemically reducing PbO to metallic lead. The devitrified seals formed by these other binders is gray or gray-black, indicating the presence of metallic lead in the seal.

Attempts have been made to overcome the tendency of the PbO constituent in seals formed by these other binders to be reduced during the sealing process. One such method, described in United States Letters Patent No. 3,973,975 to Francel *et al.*, involves the addition to the PbO-containing sealing glass frit and the sealing glass paste made therefrom of a sufficient amount of a powder of a higher oxide of a cation that is thermally stable at the temperatures at which the sealing glass frit seals the glass surfaces



together, but that can be reduced to a lower oxide of the cation when exposed to the reducing conditions. Any reducing agent in contact with such a sealing glass during the time the sealing glass is melting and sealing will tend to reduce the higher oxide of the metal to the lower oxide rather than reducing the PbO in the sealing glass to metallic lead. The addition of certain oxides, nitrates, and other oxidizing agents to the sealing glass in amounts from at least 0.1 to about 1.5% by weight of the sealing glass were shown to decrease the reduction of the PbO in the sealing glass to metallic lead and to permit the substitution of a non-nitrocellulose binder, such as hydroxypropyl cellulose, for a portion of the nitrocellulose binder. However, the addition of such oxidizing agents to the sealing glass frit did not eliminate the need for the use of at least some nitrocellulose binder.

Notwithstanding these efforts, all commercially successful vehicles for PbO-containing sealing glasses include nitrocellulose, which in turn requires the use of a volatile organic compound as a solvent for the nitrocellulose. None of the known vehicles for PbO-containing sealing glasses solves the problem of VOC emissions that result from volatilization of the vehicle.

Thus, there exists a need in the art for a sealing glass system for use as a solder glass for sealing the face plate to the funnel portion of a color television tube that is capable of being used with a VOC-free or low-VOC vehicle, and particularly an aqueous vehicle. (As used herein, the term "low-VOC vehicle" includes VOC-free formulations.) As with conventional sealing glass systems, the novel system must be resistant to substantial chemical reduction of PbO in the glass to metallic lead when the sealing glass is exposed to reducing conditions during sealing or firing and produce a seal having suitable dielectric and other properties.

This invention aids in fulfilling these needs in the art by providing a sealing glass modifier that decreases the chemical reduction of PbO to metallic lead in a VOC-free or low-VOC sealing glass system when the sealing glass is exposed to reducing conditions during sealing or firing. As used herein, the term "modifier" means any substance that can be used in an amount sufficient to prevent the PbO from being chemically reduced when the glass frit is being fired in the presence of reducing conditions at a temperature sufficient to seal the glass without having a substantial adverse effect on the properties of the sealing glass paste or the fired glass seal. The modifier comprises an inorganic nitrate that is thermally stable at the temperatures at which the sealing glass frit seals the glass surfaces together, but that can be reduced to a lower oxidation state when exposed to the reducing conditions. Any reducing agent in contact with the modified sealing glass system during the time the sealing glass is melting and sealing will tend to reduce the inorganic nitrate to its lower oxidation state rather than reducing the PbO in the sealing glass to metallic lead. Preferably, the inorganic nitrate is  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and/or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

The modifier of the present invention may be incorporated as a component of the sealing glass frit. The modified frit glass comprises a PbO-containing glass frit having a sealing or firing temperature within the temperature range of about 420° C. to about 460° C., and a modifier in an amount sufficient to prevent the PbO in the sealing glass from being chemically reduced when the glass frit is fired in the presence of reducing conditions at a temperature sufficient to seal the glass. The invention includes a sealing glass paste comprising the above-described modified frit in combination with a VOC-free or low-VOC vehicle.

The modifier also may be dissolved or dispersed in a sealing glass vehicle for a PbO-containing glass. The modified vehicle comprises a VOC-free or low-VOC vehicle and a modifier in an amount sufficient to prevent the PbO in the sealing glass from being chemically reduced when the glass is fired in the presence of reducing conditions at a temperature sufficient to seal the glass. The invention further includes a sealing glass paste comprising the above-described modified vehicle in combination with a PbO-containing glass frit having a sealing or firing temperature with the temperature range of about 420° C. to about 460° C.

In addition, the invention includes a method of sealing a face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a VOC-free or low-VOC vehicle, under conditions capable of reducing the PbO to metallic lead, comprising the steps of :

- A. Applying between the sealing edges of the face plate and funnel portions a sealing amount of the sealing glass composition of this invention; and
- B. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

Further, this invention includes a method of sealing a face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a VOC-free or low-VOC vehicle, in the presence of conditions capable of reducing the PbO to metallic lead, comprising the steps of A. Combining the sealing glass with a modifier in an amount sufficient to

prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;

- B. Applying a sealing amount of the modified sealing glass between the sealing edges of the face plate and funnel portions; and
- C. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

Still further, this invention provides a method of sealing a face plate to a funnel of a cathode ray tube using a PbO-containing sealing glass, in the presence of conditions capable of reducing the PbO to metallic lead, comprising the steps of:

- A. Combining a low-VOC vehicle with a modifier in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;
- B. Combining the modified vehicle with a sealing glass to form a sealing glass paste;
- C. Applying a sealing amount of the modified sealing glass paste between the sealing edges of the face plate and funnel portions; and
- D. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

These and other objects of the present invention will be apparent from the specification that follows and the appended claims.

### SUMMARY OF THE INVENTION

The foregoing objectives are achieved in a sealing glass modifier that enables a PbO-containing sealing glass to be used in combination with a VOC-free or low-VOC vehicle by decreasing the chemical reduction of PbO in the sealing glass to metallic lead during sealing or firing. The modifier preferably comprises an inorganic nitrate that is thermally stable at the temperatures at which the sealing glass frit seals the glass surfaces together, but that can be reduced to a lower oxidation state when exposed to the reducing conditions. Any reducing agent in contact with such a modified sealing glass system during the time the sealing glass is melting and sealing will tend to reduce the inorganic nitrate to its lower oxidation state rather than reducing the PbO in the sealing glass to metallic lead. Particularly preferred modifiers are  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and/or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The modifier is added to the sealing glass system in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired in the presence of reducing conditions at a temperature sufficient to seal the glass. The invention includes the use of a modifier in a sealing glass system to decrease the reduction of PbO during firing and sealing, a sealing glass incorporating the modifier, a sealing glass paste including the modified sealing glass, a vehicle incorporating the modifier, a sealing glass paste including the modified vehicle, the methods of making the modified sealing glass, the modified vehicle, and the related pastes, and the methods of sealing the tube components using the modified sealing glass and the modified vehicle.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)**

The present invention provides a sealing glass modifier that decreases the chemical reduction of PbO in a PbO-containing sealing glass to metallic lead during sealing or firing, and enables the sealing glass to be used in combination with a VOC-free or low-VOC vehicle. The modifier preferentially comprises bismuth nitrate and/or zinc nitrate in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired in the presence of reducing conditions at a temperature sufficient to seal the glass.

**A. Sealing Glass**

Lead-zinc-borate solder glasses are preferred in practicing this invention. Such glasses are well-known in the solder glass art, and examples can be found in United States Letters Patent No. 4,589,899 to Hudacek. The solder glasses useful in the practice of this invention also are referred to herein as the "base glass."

The lead-zinc-borate glasses suitable for use in the present invention typically have the oxide composition (as calculated from raw batch starting materials) specified in Table 1, expressed in weight percent, and wherein the total content of all oxides is 100%.

**TABLE 1. PREFERRED BASE GLASS COMPOSITION**

<b><u>Oxides</u></b>	<b><u>Usual Range</u></b>	<b><u>Preferred Range</u></b>	<b><u>Preferred Values</u></b>
PbO	70-80	73-77	75.0
B <sub>2</sub> O <sub>3</sub>	5-11	7-10	8.5
ZnO	9-16	10-14	12.5
SiO <sub>2</sub>	0- 5	1- 3	2.0
BaO	0- 3	1.5- 2.5	2.0

The particularly preferred base glass composition set forth above in the "Preferred Values" column is especially well-suited for color television picture tube applications.

Other conventional glass making oxides such as  $\text{CaO}$ ,  $\text{CuO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{CdO}$ , and  $\text{Fe}_2\text{O}_3$  can be included. However, it is preferred in many instances not to employ these constituents, but rather to provide compositions that consist essentially only of those constituents set forth in Table 1, above.

The particle size of the glass frit is not particularly critical to the practice of the present invention, and any conventional particle size distribution can be employed. Typically, the particle size of the glass frit will be such that about 100% of the particles pass a 100 mesh (U.S. Standard Sieve Series) screen, and at least about 60% of the particles pass a 400 mesh screen.

It is also preferred that the base glass used in the practice of this invention have the following properties:

- A. A glassy edge of about  $360^\circ\text{C}$ . to about  $390^\circ\text{C}$ ., preferably about  $370^\circ\text{C}$ ., as determined by a gradient boat test;
- B. A devitrification edge of about  $390^\circ\text{C}$ . to about  $425^\circ\text{C}$ ., preferably about  $415^\circ\text{C}$ ., as determined by a gradient boat test;
- C. A button flow of about 1.050 to about 1.120 inches diameter, preferably about 1.080 inches diameter; and
- D. A rod stress within the tensional stress range of about 0 p.s.i. to about 1000 p.s.i., preferably about 300 p.s.i. to about 800 p.s.i., especially about 500 p.s.i. The terms "gradient boat test," "button flow" and "rod stress value" have the same meanings and are

determined according to the same procedures set forth in United States Letters Patent No. 4,058,387 to Nofziger.

The results described herein relate to the use of the particularly preferred base glass. However, it is believed that any PbO-containing glass frit having a sealing or firing temperature within the temperature range of about 420° C. to about 460° C. can be used with satisfactory results.

**B. Vehicle**

A VOC-free vehicle that reasonably satisfies the requirements that the vehicle be capable of holding the solder glass frit in a ribbon form for a sufficient length of time for satisfactory application to the funnel surface, and that the resultant paste be stable enough that it can be made in quantities suitable for use in commercial tube manufacture, is vehicle A9065, available from Alpha Metals, Inc., Jersey City, New Jersey. This VOC-free vehicle is a colorless liquid comprising 97-98% water and less than 2% cellulose. It has a specific gravity of about 1.00 to about 1.01 and a pH in the range of about 5.0 to about 8.0. The weight ratio of sealing glass solids (including refractory fillers, nucleating agents, and modifiers) to vehicle is usually in the range of about 6.0:1 to about 12.0:1, and preferably about 8.0:1 to about 8.5:1, for a VOC-free or low-VOC vehicle such as vehicle A9065.

The results described herein relate to sealing glass systems that make use of vehicle A9065. However, it is contemplated that the invention may be practiced with other VOC-free or low-VOC vehicles having similar properties.



### C. Modifier

As described above, the modifier of the present invention preferably comprises an inorganic nitrate that is thermally stable at the temperatures at which the sealing glass frit seals the glass surfaces together, but that can be reduced to a lower oxidation state when exposed to the reducing conditions. The modifier is added to the sealing glass system in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired in the presence of reducing conditions at a temperature sufficient to seal the glass.

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and/or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are the particularly preferred modifiers. These modifiers are effective in decreasing the chemical reduction of PbO during firing and sealing of the glass without causing any substantial adverse effect on the rheology of the sealing glass paste or on the sealing properties of the base glass.

The effectiveness of a modifier in decreasing the reduction of PbO usually can be determined visually by comparing the colors of fired frits with and without the modifier. The formation of free lead or a lower oxide of lead during firing is characterized by a gray or black color appearing in the fired frit unless, of course, the modifier itself is black or gray in color. In all cases, analytical tests can be used to determine the presence of metallic lead, and therefore, the effectiveness of the modifier. The effectiveness of the modifier also may be shown by dielectric tests of the resultant seal.

Modifier candidates initially were assessed by examining the visual rheology of modified paste samples and the color of the corresponding glass frits after firing. The test samples were prepared by incorporating a modifier (in an amount equal to about 1% by weight of the base glass) in the particularly preferred PbO-containing glass frit described

above. The modified base glass samples were then combined with VOC-free vehicle A9065 by hand mixing in a weight ratio of about 8.3:1. After the sample rheology was assessed, the samples were fired at a temperature of about 420° C. to about 460° C. The samples were compared to a base glass control, which was similarly combined with the VOC-free vehicle A9065 in a weight ratio of about 8.3:1 and fired at a temperature of about 420° C. to about 460° C. The results of these tests are provided in Table 2.

TABLE 2. VISUAL ASSESSMENT OF MODIFIERS

<u>Modifier</u>	<u>Color</u>	<u>Visual Rheology</u>
Control (unmodified base glass)	Gray	Medium gelation
PbO <sub>2</sub>	Red orange	Slight or no change
Pb(NO <sub>3</sub> ) <sub>2</sub>	Ivory with beige splotches	Initially broke gel structure and gradually returned
Pb <sub>3</sub> O <sub>4</sub>	Orange-yellow	Completely gelled
Bi(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	Yellow	Initially broke gel structure
Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	Orange-yellow	No change
BaO <sub>2</sub>	Orange, porous	Gelled
C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	Black, porous	No change
Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	Yellow	Slight gel

Of the compounds tested, Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O were the most effective in decreasing the reduction of PbO to metallic lead, as evidenced by the yellow color of the fired frits. Pb<sub>3</sub>O<sub>4</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O appeared to be somewhat less effective in decreasing PbO reduction during firing of the frit. C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> was not effective in decreasing the reduction of PbO to metallic lead during firing, as evidenced by the black color of the fired frit.

Both BaO<sub>2</sub> and Pb<sub>3</sub>O<sub>4</sub> (which were among the most preferred additives in decreasing the reduction of PbO in conventional nitrocellulose binder systems) exhibited unsatisfactory visual rheology in the VOC-free vehicle system. The C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> seal had a porous appearance, which is indicative of low seal strength and an increased likelihood of dielectric breakdown.

Further tests were conducted to determine the amount of the modifier necessary to achieve the desired decrease in PbO reduction. In these tests, varying amounts of

modifiers were incorporated into the preferred PbO base glass, and the modified glasses were combined with vehicle A9065 and fired as described above. After firing, the color of the modified frits were evaluated. The results of these tests are shown in Table 3.

TABLE 3. EFFECTIVE AMOUNTS OF MODIFIERS

<u>Sample No.</u>	<u>Compound</u>	<u>Available Oxygen (%)</u>	<u>Decomposition Point (° C.)</u>	<u>Hand Mix Rheology (at 1%)</u>	<u>1.0%</u>	<u>0.25%</u>	<u>0.1%</u>
1	PbO <sub>2</sub>	6.69	290	no effect	red-orange	orange	gray-orange
2	Pb(NO <sub>3</sub> ) <sub>2</sub>	14.5	470	thin/thicken	pale yellow	beige	
3	Pb <sub>3</sub> O <sub>4</sub>	2.33	500	thicken	orange	gray-beige	
4	Bi(NO <sub>3</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	14.84	500	thin/thicken	yellow	pale yellow	gray-orange
5	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	20.33	132	no effect	orange*-bumpy	pale yellow-beige	gray-orange
6	BaO <sub>2</sub>	9.45	800	thicken	orange-porous		
7	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	?	?	no effect	black-porous		
8	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	19.72	?	slight thickener	yellow-orange	pale yellow	gray-orange

\*May have been affected by samples 6 and 7.

As shown in Table 3, the  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  modifiers achieved satisfactory results when incorporated into the base glass in amounts ranging from about 0.25% to about 1% by weight of the base glass.  $\text{PbO}_2$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  also achieved satisfactory results in these amounts based on the color of the fired frits. However, the fired frit containing  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  had a bumpy appearance, indicating that the molten paste flow was not uniform.

$\text{Pb}_3\text{O}_4$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{BaO}_2$  in an amount equal to 1% by weight of the base glass produced seals with a satisfactory color. The fired  $\text{BaO}_2$  frit, however, had a porous appearance indicative of low seal strength.  $\text{C}_4\text{H}_4\text{O}_4$  did not yield satisfactory results at any of the levels tested and had a porous appearance at the 1% level. None of the tested compounds achieved satisfactory results in an amount equal to 0.1% by weight of the base glass.

Selected compounds from Table 3 that passed the initial screening, namely,  $\text{PbO}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were further subjected to differential thermal analysis (DTA) to assess their crystallization behavior. Samples of base glass were combined with both a conventional vehicle (Vehicle F1016, 1.25% nitrocellulose in amyl acetate, in a weight ratio of about 12.5:1) and vehicle A9065 (in a weight ratio of about 8.3:1). The vehicles were driven off the samples by heat at about 300° C. to yield Sample Nos. 1 and 2, respectively. The modified blend samples were prepared by incorporating the modifier, combining the modified base glass with vehicle A9065 in a weight ratio of about 8.3:1, and driving the vehicle off by heat at about 300° C. as described above for Sample No. 2.

The DTA results for the modified blend samples were compared to those for the base sealing glass powder (Sample #8), which was used as the base glass in all samples, and the samples prepared from the base glass with the conventional vehicle (Sample #1) and with vehicle A9065 (Sample #2). The DTAs on all of the dried pastes and the sealing glass powder (Sample #8) were conducted using the following thermal cycle: increasing the temperature at a rate of about 10° C./minute to about 440° C., and holding at this temperature for 60 minutes or until the thermal curve was complete. The results of these tests are shown in Table 4.

TABLE 4. CRYSTALLIZATION BEHAVIOR OF MODIFIED FRITS

<u>Sample No.</u>	<u>Vehicle</u>	<u>Additive</u>	<u>Additive %</u>	<u>DTA-Peak (minutes)</u>	<u>DTA-Complete (minutes)</u>	<u>Completion-Peak</u>	<u>Button Flow (inches)</u>
1	F1016 @12.5:1	None	0	27.1	31.9	4.8	1.072
2	A9065 @ 8.3:1	None	0	24.6	30.0	5.4	1.075
3	A9065 @ 8.3:1	PbO <sub>2</sub>	0.3	22.5	35.2	12.7	1.086
4	A9065 @ 8.3:1	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.4	21.5	26.2	4.7	1.068
5	A9065 @8.3:1	Bi(NO <sub>3</sub> ) <sub>3</sub> 5H <sub>2</sub> O	0.3	27.5	32.1	4.6	1.083
6	A9065 @ 8.3:1	Ca(NO <sub>3</sub> ) <sub>2</sub> 4H <sub>2</sub> O	0.3	30.3	35.5	5.2	1.092
7	A9065 @ 8.3:1	Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O	0.3	27.4	31.8	4.4	1.061
8	None (powder)	None	0	27.9	32.69	4.7	1.085



A satisfactory modifier should result in little, if any, change in the DTA crystallization characteristics of the modified glass compared to the unmodified sealing glass powder (Sample #8). As can be seen from Table 4, dried paste using the standard vehicle system (Sample #1) showed only slight differences between the DTA peak and DTA completion time when compared to sealing glass powder (Sample #8).

Unmodified dried paste using the VOC-free vehicle Alpha A9065 (Sample #2) showed a slightly faster DTA peak and DTA completion than sealing glass powder (Sample #8).

Dried paste using a  $\text{PbO}_2$  modifier (Sample #2) showed a significantly faster DTA peak time and a significantly slower completion time compared to sealing glass powder (Sample #8). This sample also exhibited unsatisfactory crystallization behavior as evidenced by the absence of a sharp peak and a smooth curve from peak to completion on the DTA plot for this sample. Dried paste using a  $\text{Pb}(\text{NO}_3)_2$  modifier showed a significantly faster DTA peak time and completion time than sealing glass powder (Sample #8). These results indicate an unsatisfactorily fast crystallization rate for the  $\text{Pb}(\text{NO}_3)_2$  - modified paste.

Dried paste using either  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (Sample # 5) or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sample #7) as the modifier showed only very slight differences in the DTA peak time or DTA completion time compared to sealing glass powder (Sample #8). These modifiers exhibited the least influence on the DTA crystallization characteristics of the sealing glass powder. Dried paste using a  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  modifier (Sample #6) showed a slightly slower DTA peak time and DTA completion time than sealing glass powder (Sample #8).

The amount of the modifier used to prevent or decrease the chemical reduction of the PbO will depend, among others things, upon the relative effectiveness of the modifier and the conditions to which the sealing glass is exposed during sealing and firing. The foregoing description of the relative effectiveness of modifiers, when employed with the particularly preferred base glass, can be used as a guide for this purpose. The effective amount of the modifier typically will be in the range of about 0.05 to about 5 weight percent of the sealing glass, and preferably in an amount of about 0.1 to about 1.0 weight percent of the sealing glass. Although amounts in excess of 1.0 weight percent were not tested, it is believed that higher amounts also will yield satisfactory results; provided, however, that these amounts are not so high that they adversely affect the other properties of the sealing glass system. Optimum performance of the sealing glass is obtained when the modifier is added in an amount that is not greatly in excess of the effective amount. This minimizes adverse effects on the rheology of the sealing glass paste and the sealing properties (including crystallization behavior) of the base glass.

The particularly preferred modifiers  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are typically employed in an amount of about 0.25 to about 1 weight percent of the sealing glass composition, and preferably about 0.3 to about 0.5 weight percent, when used with the particularly preferred base glass and Alpha Metals vehicle A9065 in a ratio of about 8.3:1. With improved low-VOC vehicles, however, it is expected that satisfactory results may be achieved by using the modifier of the present invention in an amount as low as about 0.05% by weight of the base glass.

Commercial grades of the preferred modifiers have been found to be suitable for use in this invention. These modifiers of the present invention have been found to perform satisfactorily in the hydration states specified above; however, the hydration states are not thought to be critical, and it is expected that these modifiers would yield satisfactory results in other hydration states as well.

One way in which the modifier may be used in a sealing glass system is by substituting the modifier for a portion of the frit. Optimum results may be obtained by reducing the particle size of the modifier and distributing it evenly throughout the sealing glass powder. This may be accomplished, for example, using the two-step process described below. In the first step, about 10% to about 20% of the modifier in sealing glass powder is blended in a twin shell or rotocone blender for about 5 to about 15 minutes. In the second step, the blended material from Step 1 is placed into a ceramic lined ball mill with ceramic grinding media and ground for about 5 to about 30 minutes. The material from Step 2 is referred to as a modifier masterblend. A desired amount of the modifier masterblend may be uniformly dispersing in the final sealing glass product, for example, using a rotocone blender.

A sealing glass paste of the present invention may be prepared by mixing the modified sealing glass blend with a VOC-free or low-VOC vehicle, in conventional manner. The weight ratio of sealing glass solids (including refractory fillers, nucleating agents, and modifiers) to vehicle is usually in the range or about 7.0:1 to about 13.0:1, and preferably about 8.0:1 to about 8.5:1. A mixing time of not more than about thirty minutes is recommended to prolong the useful life of the paste.

The modified vehicle of this invention may be prepared by dissolving an appropriate amount of the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  modifier into the commercially available A9065 vehicle, and using the vehicle to prepare a sealing glass paste in the conventional manner. This is a particularly easy and economical way to incorporate the modifier into the sealing glass system. Although the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  modifier is preferred for preparation of a modified vehicle because of its solubility in the vehicle, it also is possible to prepare the modified vehicle by dispersing the appropriate quantity of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in the vehicle. However, the  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ -containing vehicle requires agitation before use in preparation of a sealing glass paste to rehomogenize the vehicle and provide a uniform distribution of the  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  dispersed therein. The amount of modifier added to the vehicle to create the modified vehicle generally will be in the range of about 0.005% to about 0.1% by weight of the vehicle.

Another sealing glass paste of the present invention may be prepared by mixing the modified vehicle, prepared as described above, with the base sealing glass. As with the other sealing glass paste, the weight ratio of sealing glass solids to vehicle is usually in the range or about 7.0:1 to about 13.0:1, and preferably about 8.0:1 to about 8.5:1, and a mixing time of not more than about thirty minutes is recommended.

The present invention includes a method of sealing a face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a VOC-free or low-VOC vehicle, under conditions capable of reducing the PbO to metallic lead, comprising the steps of :

- A. Applying between the sealing edges of the face plate and funnel portions a sealing amount of the sealing glass composition of this invention; and

B. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

Further, this invention includes a method of sealing a face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a VOC-free or low-VOC vehicle, under conditions capable of reducing the PbO to metallic lead, comprising the steps of :

- A. Combining the sealing glass with a modifier in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;
- B. Applying a sealing amount of the modified sealing glass between the sealing edges of the face plate and funnel portions; and
- C. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

Still further, this invention provides a method of sealing a face plate to a funnel portion of a cathode ray tube, such as a color television tube, with a PbO-containing sealing glass, comprising the steps of:

- A. Combining a VOC-free or low-VOC vehicle with a modifier in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;

- B. Combining the modified vehicle with a sealing glass to form a sealing glass paste;
- C. Applying a sealing amount of the modified sealing glass paste between the sealing edges of the face plate and funnel portions; and
- D. Subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

At present, sealing glass pastes made with a VOC-free vehicle such as A9065 from Alpha Metals do not achieve the rheology and shelf life characteristics (with or without the presence of modifiers) of sealing glass paste made with conventional vehicles comprising nitrocellulose in amyl or butyl acetate. Typical pastes made with the conventional vehicle system have a stable rheology for about 0.5 to about 8 hours after mixing in a typical tube manufacturing plant. The shelf life of such pastes is usually up to about 48 hours after mixing. Pastes made with a VOC-free vehicle such as A9065, with or without modifiers, currently are stable up to about 2 hours after mixing. The shelf life of these VOC-free pastes does not exceed about 4 hours unless additional vehicle is added to the paste with subsequent mixing. In short, available VOC-free pastes have commercially useful, but not optimal rheology and shelf-life characteristics. Nevertheless, it is believed that some tube manufacturers may be willing to adjust their mixing and dispensing processes to accommodate these characteristics of VOC-free pastes because of the environmental benefits of VOC-free sealing glass systems.

Although specific embodiments of the invention have been described herein in detail, it is understood that variations may be made thereto by those skilled in the art without departing from the spirit of the invention or the scope of the appended claims.

\* \* \* \* \*

What is claimed is:

1. A modifier for use in combination with a PbO-containing sealing glass and a low-VOC sealing glass vehicle for sealing the face plate to the funnel of a cathode ray tube, said modifier decreasing the chemical reduction of the PbO-constituent in the sealing glass during firing of the sealing glass.
2. The modifier according to Claim 1, wherein the amount of the modifier used is at least about 0.05 percent of the weight of the sealing glass.
3. The modifier according to Claim 1, wherein the amount of the modifier used is about 0.05 to about 5.0 weight percent of the sealing glass.
4. The modifier according to Claim 1, wherein the amount of the modifier is about 0.05 to about 1.0 weight percent of the sealing glass.
5. The modifier according to Claim 1, wherein the amount of the modifier is about 0.1 to about 0.5 weight percent of the sealing glass.
6. The modifier according to Claim 1, wherein the amount of the modifier is about 0.25 to about 0.5 weight percent of the sealing glass.



7. The modifier according to Claim 1, wherein the amount of the modifier is about 0.3 to about 0.8 weight percent of the sealing glass.

8. The modifier according to Claim 1, wherein said modifier comprises bismuth nitrate.

9. The modifier according to Claim 1, wherein said modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .

10. The modifier according to Claim 9, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the sealing glass.

11. The modifier according to Claim 9, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the sealing glass.

12. The modifier according to Claim 9, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the sealing glass.

13. The modifier according to Claim 9 wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the sealing glass.

14. The modifier according to Claim 9, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.2 to about 0.5 weight percent of the sealing glass.

15. The modifier according to Claim 9, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.3 to about 0.8 weight percent of the sealing glass.
16. The modifier according to Claim 1, wherein said modifier comprises zinc nitrate.
17. The modifier according to Claim 1, wherein said modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .
18. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the sealing glass.
19. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the sealing glass.
20. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the sealing glass.
21. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the sealing glass.
22. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.25 to about 0.5 weight percent of the sealing glass.

23. The modifier according to Claim 16, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.3 to about 0.8 weight percent of the sealing glass.

24. The modifier according to Claim 1, said modifier further causing the seal formed between the face plate and the funnel to exhibit acceptable dielectric properties.

25. A composition in powdered form for sealing the face plate and the funnel of a cathode ray tube, said composition comprising:

a crystallizable  $\text{PbO}/\text{ZnO}/\text{B}_2\text{O}_3$  glass; and

a modifier, said modifier decreasing the chemical reduction of the  $\text{PbO}$ -constituent in the crystallizable glass during sealing of the cathode ray tube components.

26. The composition according to Claim 25, wherein said modifier comprises bismuth nitrate.

27. The composition according to Claim 25, wherein said modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .

28. The composition according to Claim 25, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the crystallizable glass.

29. The composition according to Claim 25, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the crystallizable glass.
30. The composition according to Claim 25, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the crystallizable glass.
31. The composition according to Claim 25 wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the crystallizable glass.
32. The composition according to Claim 25, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.25 to about 0.5 weight percent of the crystallizable glass.
33. The composition according to Claim 25, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.3 to about 0.8 weight percent of the crystallizable glass.
34. The composition according to Claim 25, wherein said modifier comprises zinc nitrate.
35. The composition according to Claim 25, wherein said modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .
36. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the crystallizable glass.

37. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the crystallizable glass.

38. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the crystallizable glass.

39. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the crystallizable glass.

40. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.25 to about 0.5 weight percent of the crystallizable glass.

41. The composition according to Claim 35, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.3 to about 0.8 weight percent of the crystallizable glass.

42. The composition according to Claim 25, wherein said  $\text{PbO}/\text{ZnO}/\text{B}_2\text{O}_3$  glass comprises the following ingredients in approximate percent by weight:

<u>Ingredient</u>	<u>Percent By Weight</u>
PbO	70 to 80
ZnO	5 to 11
$\text{B}_2\text{O}_3$	9 to 16
$\text{SiO}_2$	0 to 5

43. A vehicle for use in combination with a PbO-containing sealing glass for sealing the face plate to the funnel of a cathode ray tube, said vehicle comprising:

a low-VOC liquid; and

a modifier, said modifier decreasing the chemical reduction of the PbO-constituent in the sealing glass during firing of the sealing glass.

44. The vehicle according to Claim 43, wherein said modifier is dissolved in the low-VOC liquid.

45. The vehicle according to Claim 44, wherein said modifier is  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

46. The vehicle according to Claim 45, wherein said  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is present in the vehicle in an amount from about 0.005 to about 0.1 weight percent of the vehicle.

47. The vehicle according to Claim 43, wherein said modifier is dispersed in the low-VOC liquid.

48. The vehicle according to Claim 47, wherein said modifier is  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .

49. The vehicle according to Claim 48, wherein said  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is present in the vehicle in an amount from about 0.005 to about 0.1 weight percent of the vehicle.

50. A sealing glass paste for sealing the face plate and the funnel of a cathode ray tube, said composition comprising:

a crystallizable  $\text{PbO}/\text{ZnO}/\text{B}_2\text{O}_3$  glass in powdered form;

a modifier, said modifier decreasing the chemical reduction of the  $\text{PbO}$ -constituent in the crystallizable glass during sealing of the cathode ray tube components; and

a low-VOC liquid capable of holding the powdered glass in ribbon form for a period of time sufficient to enable the resultant paste to be applied to a surface of one of the cathode ray tube components.

51. The sealing glass paste according to Claim 50, wherein said modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

52. The sealing glass paste according to Claim 51, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the powdered glass.

53. The sealing glass paste according to Claim 51, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the powdered glass.

54. The sealing glass paste according to Claim 51, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the powdered glass.

55. The sealing glass paste according to Claim 51, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the powdered glass.

56. The sealing glass paste according to Claim 50, wherein the modifier is soluble in the low-VOC liquid.

57. The sealing glass paste according to Claim 50, wherein said modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .

58. The sealing glass paste according to Claim 57, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the powdered glass.

59. The sealing glass paste according to Claim 57, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the powdered glass.

60. The sealing glass paste according to Claim 57, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the powdered glass.

61. The sealing glass paste according to Claim 57, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the powdered glass.

62. A method of making a sealing glass paste for sealing the face plate and the funnel of a cathode ray tube, said method comprising the steps of:



providing a crystallizable  $\text{PbO}/\text{ZnO}/\text{B}_2\text{O}_3$  glass in powdered form;

providing a modifier, said modifier decreasing the chemical reduction of the  $\text{PbO}$ -constituent in the crystallizable glass during sealing of the cathode ray tube components;

incorporating said modifier into said powdered glass to form a sealing glass blend; and

mixing said sealing glass blend with a VOC-free vehicle, said vehicle holding the sealing glass blend in ribbon form for a period of time sufficient to enable the resultant paste to be applied to a surface of one of the cathode ray tube components.

63. The method according to Claim 62, wherein the modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

64. The method according to Claim 63, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the powdered glass.

65. The method according to Claim 63, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the powdered glass.

66. The method according to Claim 63, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the powdered glass.

67. The method according to Claim 63, wherein the amount of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the powdered glass.
68. The method according to Claim 62, wherein the modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .
69. The method according to Claim 68 wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is at least about 0.05 percent of the weight of the powdered glass.
70. The method according to Claim 68, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 5.0 weight percent of the powdered glass.
71. The method according to Claim 68, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.05 to about 1.0 weight percent of the powdered glass.
72. The method according to Claim 68, wherein the amount of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is about 0.1 to about 0.5 weight percent of the powdered glass.
73. The method according to Claim 62, wherein the weight ratio of sealing glass solids to vehicle is in the range of about 7.0:1 to about 13.0:1.
74. The method according to Claim 62, wherein the weight ratio of sealing glass solids to vehicle is in the range of about 8.0:1 to about 8.5:1.

75. The method according to Claim 62, wherein the step of incorporating the modifier into the powdered glass includes the step of grinding the modifier and the powdered glass.

76. The method according to Claim 62, wherein the mixing time is less than about thirty minutes.

77. A method of making a sealing glass paste for sealing the face plate and the funnel of a cathode ray tube, said method comprising the steps of:

providing a low-VOC vehicle, said vehicle capable of holding a powdered sealing glass in ribbon form for a period of time sufficient to enable the resultant paste to be applied to a surface of one of the cathode ray tube components;

combining said vehicle with a modifier to form a modified vehicle, said modifier decreasing the chemical reduction of the PbO-constituent in the crystallizable glass during sealing of the cathode ray tube components;

providing a powdered PbO/ZnO/B<sub>2</sub>O<sub>3</sub> sealing glass; and

mixing said modified vehicle and said sealing glass to form a paste.

78. The method according to Claim 77, wherein the step of combining the vehicle with the modifier further includes the step of:

dissolving an appropriate quantity of the Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O modifier in the vehicle.

79. The method according to Claim 77, wherein the step of combining the vehicle with the modifier further includes the steps of:

dispersing an appropriate quantity of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in the vehicle; and  
agitating the modified vehicle before combining it with the sealing glass.

80. A method of sealing the face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a low VOC vehicle, under conditions capable of reducing the PbO to metallic lead, comprising the steps of:

preparing a modified sealing glass composition;  
applying between the sealing edges of the face plate and funnel portions a sealing amount of the sealing glass composition; and  
subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

81. The method according to Claim 80, wherein the step of preparing a modified sealing glass composition comprises the steps of:

providing a crystallizable  $\text{PbO}/\text{ZnO}/\text{B}_2\text{O}_3$  glass in powdered form;  
providing a modifier, said modifier decreasing the chemical reduction of the PbO-constituent in the crystallizable glass during sealing of the cathode ray tube components;

incorporating said modifier into said powdered glass to form a sealing glass blend; and

mixing said sealing glass blend with a VOC-free vehicle, said vehicle holding the sealing glass blend in ribbon form for a period of time sufficient to enable the resultant paste to be applied to a surface of one of the cathode ray tube components.

82. The method according to Claim 81, wherein the modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in an amount from about 0.3 to about 1.0 weight percent of the powdered glass.

83. The method according to Claim 81, wherein the modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in an amount from about 0.3 to about 1.0 weight percent of the powdered glass.

84. A method of sealing a face plate to the funnel of a cathode ray tube using a PbO-containing sealing glass in a low VOC vehicle, under conditions capable of reducing the PbO to metallic lead, comprising the steps of :

combining the sealing glass with a modifier in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;

applying a sealing amount of the modified sealing glass between the sealing edges of the face plate and funnel portions; and

subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

85. A method of sealing the face plate to the funnel of a cathode ray tube with a PbO-containing sealing glass, comprising the steps of:

combining a low-VOC vehicle with a modifier in an amount sufficient to prevent the PbO from being chemically reduced when the sealing glass is fired at a temperature sufficient to seal the glass;

combining the modified vehicle with a sealing glass to form a sealing glass paste;

applying a sealing amount of the sealing glass paste between the sealing edges of the face plate and funnel portions; and

subjecting the applied sealing glass composition to a sealing temperature within the sealing temperature range of between about 420° C. and about 460° C. for a period of time sufficient to fuse said sealing glass composition and form a seal to and between the sealing edges of the face plate and funnel portions.

86. The method according to Claim 85, wherein the modifier comprises  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in an amount from about 0.005 to about 0.1 weight percent of the vehicle.

87. The method according to Claim 85, wherein the modifier comprises  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in an amount from about 0.005 to about 0.1 weight percent of the vehicle.

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